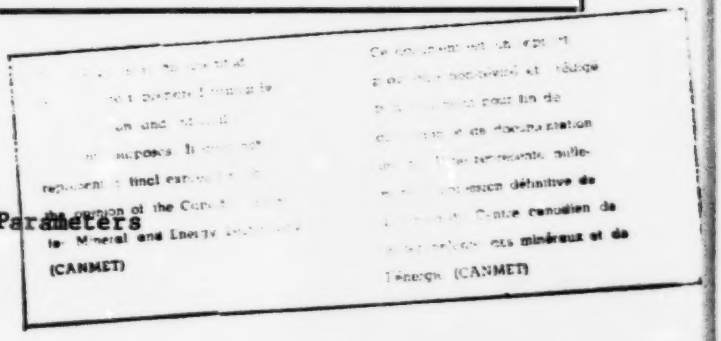
Energy, Mines and Resources Canada
Énergie, Mines et Ressources Canada

CANMET
Canada Centre for Mineral and Energy Technology
Centre canadien de la technologie des minéraux et de l'énergie

METHODS TO IMPROVE LIMESTONE UTILIZATION IN FLUIDIZED BEDS

C.A. Hamer
Mineral Processing Laboratory

July 1984



Project ERP-4.3.4.1.01
Combustion and Emission Abatement Parameters

MICROMEDIA
SEP 24 1984

ENERGY RESEARCH PROGRAM
MINERAL SCIENCES LABORATORIES
DIVISION REPORT ERP/MSL 84-77 (IR)

METHODS TO IMPROVE LIMESTONE UTILIZATION IN FLUIDIZED BEDS

by

C.A. Hamer

ABSTRACT

Limestone and dolomites rock samples, which had been previously evaluated as SO_2 sorbents for fluidized-bed combustors, were subjected to techniques to improve their capacity to capture sulphur. Finely ground rock was pelletized and evaluated in a bench scale fluidized-bed reactor. The increase in the sulphation capacity of pellets was as much as five times that of natural rock. Similar improvements were observed by hydrating partially sulphated bed material and also by crushing and pelletizing used bed material. An economic evaluation indicated that pelletizing is a viable method of improving limestone utilization.

MÉTHODES POUR AMÉLIORER L'UTILISATION DES CALCAIRES DANS LES LITS FLUIDISÉS

par

C.A. Hamer*

RÉSUMÉ

Des échantillons de calcaire et de dolomie, dont on avait déjà évalué les performances à titre d'absorbants de SO_2 pour la combustion en lit fluidisé, ont été traités pour améliorer leur pourvoir de rétention de soufre. La roche finement broyée et agglomérée en boulettes a été évaluée dans un réacteur à lit fluidisé en banc d'essai. On a constaté que le pourvoir de sulfatation des boulettes était cing fois plus élevé que celui des échantillons de roche à l'état naturel. Des améliorations similaires ont été obtenues par l'hydratation du lit partiellement sulfaté ainsi que par le broyage et le bouletage du lit épuisé. Selon une évaluation économique, le bouletage constitue une méthode viable d'améliorer l'utilisation du calcaire.

INTRODUCTION

A previous report discussed the utilization of limestones and dolomites as SO_2 sorbents in the atmospheric fluidized bed combustion (AFBC) of coal (1). Twenty nine calcium carbonate rocks from Nova Scotia, New Brunswick and Alberta were evaluated in a bench scale fluidized bed reactor (FBR) to determine their sulphation capacity. The test results were used in the Argonne National Laboratory model to predict the behaviour of these materials in operational AFBC units. The sorbents performance varied from very good to very poor; the best requiring about 0.5 kg limestone/kg 4% sulphur coal to achieve 90% SO_2 retention and the poorest being considered unuseable because of the excessive quantity of limestone which would be required.

Also discussed in that report were methods to improve the performance of sorbents. One such method is the agglomeration or pelletization of finely ground carbonate rock. As sulphation capacity increases with decreasing particle size, the use of fine particles greatly enhances limestone utilization. However, fine particles added to an AFBC will be immediately eleutriated from the bed by the fluidizing air. Agglomeration of the particles into pellets overcomes this problem. Pelletizing also offers the opportunity to incorporate salts or catalysts with the sorbent to further improve sulphation capacity.

Present practice in AFBC is to feed limestone in the size range 3-0.5 mm. The sulphation reaction takes place at the surface and in the pores of the sorbent material and, because the calcium sulphate reaction product has a larger molar volume than calcium carbonate, it seals the particle such that the center core remains essentially unreacted lime. The degree of conversion of calcium oxide to the sulphate is usually in the range 10-40%, the mid-twenties being common. Thus about 75% of the calcium content in the limestone is not utilized in the AFBC. This partially sulphated spent bed material can be pulverized to expose unreacted lime, pelletized and reused to increase the overall limestone utilization.

Another approach to increasing the utilization of limestone is to hydrate the spent bed material (2). Water permeates the calcium sulphate layer and reacts with the calcium oxide to form calcium hydroxide. The hydroxide, having a larger molar volume than the lime, swells and cracks

the sulphate shell. Upon reinjection of this material in a fluidized bed it dehydrates thus exposing unreacted lime for further sulphation.

In a newer fluidized bed technology, known as the circulating fluidized-bed, the limestone feed particle size is much finer than the AFBC. The superficial air velocity is several times higher such that the particles circulate from the turbulent bed through a cyclone back to the bed. There are various designs but all use finely ground limestone which greatly increases sulphation capacity. It is reasonable to believe that the sulphation behaviour of fine particle limestone pellets evaluated in this report will be indicative of the expected performance of fine limestone in a circulating fluidized bed.

This report is an investigation of some methods to improve limestone efficiency. Specifically, it describes the pelletization and sulphation testing of sorbents which had been previously evaluated as natural rock and reported in 1. Some work is described on the re-use of sulphated bed material from the Summerside AFBC.

EXPERIMENTAL PROCEDURE

PELLETIZATION

The limestone and dolomites evaluated in this work were described in (1). The samples had been prepared by crushing, grinding in a disc pulverizer and sieving. The -149 μm (100 mesh) size fraction was the feedstock for the pellets. The actual size distribution of this fraction varied from sample to sample, being dependent to some extent on the hardness of the rock. Table 1 gives the particle size distribution for several samples as determined with a Leeds and Northrup Microparticle Analyser. The volume mean diameter of limestone samples ranged from 25 to 80 μm. Dolomite samples were noticeably coarser, being in the order of 80 μm.

TABLE 1. Particle size distribution of carbonate rocks, μm

Size μm	NB-3	NS-5	NS-7	NB-4	NS-9
176	16.8	2.4	1.5	.0	6.0
125	26.2	11.6	10.4	7.2	14.7
88	21.9	9.8	11.5	8.5	14.0
62	13.1	9.7	12.1	5.2	13.4
44	5.6	7.5	10.9	7.3	4.2
31	3.7	5.4	9.9	8.5	5.0
22	5.5	10.2	9.4	8.3	5.5
16	.0	8.9	7.5	9.2	7.4
11	3.0	8.1	7.4	11.2	4.5
7.8	.0	7.0	6.1	9.0	3.4
5.5	.4	6.1	4.0	8.3	8.0
3.9	3.4	5.6	3.0	7.1	6.3
2.8	.0	7.1	5.6	9.6	7.0
vol mean	81.0	37.8	39.5	27.1	48.7

A 40-cm diameter (16-in) disc pelletizer was used to produce all the pellets. A very fine spray, or mist, of liquid for binding pellets was achieved with an air pressurized container and an atomizer nozzle. A vibratory feeder was used to regulate the limestone feed to the rotating disc.

For the bench scale reactor tests fairly small pellets were desired, 0.841-1.00 mm, as this is the standard particle size used in the sulphation evaluation. The disc pelletizer produced a variety of sizes approximately 5 mm and smaller. Large pellets which formed were crushed by hand during the operation. Normally 0.5-1.0 kg was pelletized for each limestone sample and at the completion of material feeding the pellets were allowed to roll on the disc for a further 10 minutes to improve their compaction.

The moisture content of the green pellets was measured on a moisture determination balance. Moisture was found to range between 10% and 14%. Pellets were oven dried at 85°C overnight and then sieved to provide the sized material for sulphation testing. Occasionally, when there was an insufficient quantity of 1.00-0.841 mm pellets, larger pellets were crushed in a disc pulverizer and sieved to provide broken pellets in the desired size range.

Several types and amounts of binders were used in this test series. The most commonly used dry binder was bentonite, although portland cement, quick-set cement, and plaster of paris were also tried. In each case the

binder was blended with the limestone prior to pelletizing. Sodium carbonate solution was also used as a binder and was sprayed as a fine mist onto the disc where the limestone was feed introduced.

Three samples of spent bed material from the Summerside AFBC unit were pulverized and pelletized. The samples were not fresh and had partially hydrolized such that by itself the material made fairly weak pellets. Stronger pellets were obtained when 2% bentonite or 5% Na_2CO_3 solution was added as a binder.

PELLET TESTS

The most important characteristics of good pellets are: a) load-carrying capacity or strength, b) resistance to thermal shock, and c) abrasion resistance (2). During the making of the pellets on the disc, green pellets were subjected to a drop test from about 45 cm onto a steel plate or the floor. This was a qualitative test as no set number of drops before breaking was determined. After drying, the pellets were tested for compressive strength in an Allis Chalmers Pelletester. Ten samples, in a sieved size range of 3.36-4.76 mm, were tested for each batch of pellets. The resistance to thermal shock and abrasion were qualitatively evaluated by observing the quantity of dust collected in the cyclone during a sulphation test run. Normally this quantity was small and, as it could be contaminated with some fine silica sand bed material, it was not weighed.

HYDRATION

In a preliminary experiment on hydration enhancement of sorbents, a half dozen samples of 0.841-1.00 mm limestone were sulphated in the fluidized bed reactor. This material was separated from the sand bed by sieving; the sand being slightly finer than the rock. The sulphated limestone was then allowed to soak in water at room temperature for approximately one day, after which it was placed in an 95°C oven until all the unreacted water was evaporated. The hydrated samples were reinjected into the reactor and sulphated until the emission curve indicated that the reaction was complete. The bed material was again separated from the sand bed by sieving and submitted for chemical analysis to determine the overall sulphation conversion.

In a second experiment 30-g samples of limestone were sulphated, sampled for analysis, then the remainder was hydrated, dried and re-sulphated.

SULPHATION TEST

Sulphation tests were conducted in a bench scale fluidized bed reactor. The reactor is an externally heated stainless steel pipe, 53 mm diameter by 1400 mm high, with a porous silica disc as a distributor located 350 mm from the bottom. For each test the reactor, with a bed of 250 g ASTM C109 silica sand fluidized by air, was heated to 850°C. The air was turned off and synthetic flue gas, 0.3% SO_2, 8% CO_2, 5% O_2, balance N_2, was then admitted to the reactor. Ten grams of limestone, sieved at 0.841-1.000 mm, were injected into the fluidized bed. The SO_2 in the exhaust gas was continuously analysed by a Beckman Infrared Analyser. Within a minute of adding the sample the SO_2 concentration in the exit gas dropped to a fraction of the inlet concentration. It then began to increase, the rate of increase being dependent upon the sulphation characteristics of the limestone, until after one to three hours the exhaust concentration was constant at or very near to the inlet concentration. As the area above this curve represents the SO_2 captured by the sorbent it is possible, using Simpson's Rule, to calculate the per cent sulphation versus time for the sample. A reiterative non-linear least squares computer program fits the following empirical equation to the sulphation data:

$$X(\%) = a[1-\exp(-kt^n)] \qquad \text{Eq. 1}$$

The parameters a, k and n are used for modelling. A more detailed description of this procedure is given in (1).

RESULTS AND DISCUSSION

PELLET CHARACTERISTICS

The essential criterion of pellet quality is its ability to survive handling, storage and use in a fluidized bed combustor. These are reflected in the pellet strength, abrasion resistance and resistance to

thermal shock. The pellet compressive strength was measured with a Pelletester, some of the results of the successful binders being given in Table 2. Neither plaster of paris nor portland cement produced pellets that were strong enough to warrant further testing. Quick-set cement produced strong pellets however material costs in the order of $50/tonne pellets were considered too high for this binder to be of practical use. The quantity of bentonite was experimentally found to be optimum at about 2% with NB-1 limestone. Increasing the binder content above this did not appreciably increase the pellet strength. The optimum quantity of binder would probably vary with the limestone source and particle size.

Two sodium carbonate solution concentrations were tested as binders: a 5% solution and a saturated solution which was approximately 10%. The pellets made with the more concentrated solution were stronger; however as the 5% Na_2CO_3 solution produced pellets of satisfactory strength, this concentration was used for the tests. On a dry basis the concentration of Na_2CO_3 in the pellet was approximately 1.3%.

TABLE 2. Pellet strength test
Average of ten tests per sample, 3.36-4.76 mm pellets

Sample	2% bentonite		5% Na_2CO_3 sol'n	
	Force (N) 4.06 mm	S.D.	Force (N) 4.06 mm	S.D.
NS-1	3.2	1.5	-	-
NS-2	1.9	.4	2.6	1.0
NS-3	1.5	.5	-	-
NS-4	2.4	1.3	4.6	.4
NS-5	2.0	.4	3.0	.6
NS-6	-	-	1.4	.5
NS-7	-	-	1.1	.3
NS-8	2.9	2.0	3.1	.4
NS-9	3.7	1.1	5.7	.8
NB-1	-	-	3.9	.7
NB-2	2.3	.9	2.4	.4
NB-3	-	-	2.4	.7
NB-4	1.8	1.6	4.7	.8
NB-5	3.3	.4	-	-
CS-1	-	-	3.6	.3
SY-2	2.4	.8	5.4	.5
SA-2	2.5	.8	26.1	3.0

Although not all samples were pelletized with all binders, it can be seen that there is considerable variation in the compressive strengths measured. On average, samples with sodium carbonate as a binder are stronger than those with bentonite. There is also more consistency within the replicate tests as indicated by the smaller standard deviation (S.D.) for the sodium carbonate binder. It is not known whether this test is an accurate measure of pellet performance in actual plant service. According to Tonry it is not considered to be of major importance (3). Presumably the higher the strength, the better the pellet performance. The crushing strength is of course proportional to the diameter of the pellet. Figure 1 gives the strength versus diameter for pellets bound with 15% quick-set cement. The quantity of binder is greater than would be used in practise but it certainly produced very strong pellets. The material was considered too expensive to investigate in depth.

No specific test was devised or used to measure attrition or decrepetation due to thermal shock. An indication of the breakdown of pellets in the fluidized bed is given by the quantity of cyclone dust collected. In no case was the quantity of dust considered excessive. During sulphation in the fluidized bed the formation of calcium sulphate at the surface of the pellet actually increases its strength and subsequent resistance to attrition.

SULPHATION CAPACITY

The sulphation behaviour of the pelletized limestones and dolomites was determined with the same procedure used for natural rock and detailed in (1). The improvement in the sulphation capacity of the pellets compared with the natural rock is quite dramatic, the increase being from about two- to fivefold. In fact, all of the pelletized rocks would be classified as excellent sorbents for SO_2 in FBC. Table 3 gives the sulphation capacity of the natural rock and of pellets made with bentonite and sodium carbonate binders.

The sulphation capacity of the pelletized material does not appear to bear any relationship to the capacity as natural rock. For example, the Havelock limestone, NB-1, which is a good sorbent, increases from 30% as rock to 55% as pellets. Brookfield limestone, NS-4 and 8, which is totally unacceptable as a sorbent in coarse sizes, 14-16% capacity, is an excellent sorbent, 60+ %, when finely ground and pelletized.

The material pelletized with sodium carbonate binder tends to have higher sulphation capacities than those with bentonite, although this is not always the case. In some samples the improvement with sodium carbonate binder is more than 50% greater than with bentonite. Part of the difference may be attributable to the difference in strength or abrasion resistance of the two binders; sodium carbonate being the stronger and presumably more resistant to loss of material due to attrition. The alkali itself may be beneficial as evidenced by the work at Argonne National Laboratory where sodium carbonate addition to limestone improved performance (4,5). They postulate that when salt-treated limestone is heated above 700°C, trace amounts of liquid form which increase the mobility of ions in the CaO matrix. The higher mobility via surficial liquid films enhances crystallization of CaO and $CaSO_4$ and results in the formation of large pores, with its enhanced sulphation capacity, at the expense of small ones.

TABLE 3. Sorbent sulphation capacity of carbonate rocks and pellets, 0.841-1.00 mm material

Sample		Rock	Volume Mean dia μm	Pellets	
				2% bentonite	5% Na_2CO_3
NS-1	Irish Cove	25.1	50.7	35.5	-
-9	Irish Cove	23.2	48.7	56.6	57.6
-2	Kelly Cove	23.9	-	37.5	37.1
-4	Brookfield	14.8	-	-	67.9
-8	Brookfield	16.4	34.1	60.7	67.2
-5	Calpo	31.6	37.8	53.9	50.7
-6	Glencoe	20.3	53.3	41.7	33.6
-7	Glencoe	20.5	39.5	34.2	47.0
-11	Glencoe	19.6	-	33.3	-
NB-1	Havelock	30.6	33.7	52.2	56.2
-2	Carlsile	23.5	-	-	59.0
-3	Brookfield	24.3	81.0	31.1	65.7
-4	Elm Tree	17.2	27.1	40.0	63.5
-5	Windsor	24.0	-	41.9	67.1
GR	Gays River		-	79.3	88.8
SY-2	Syncrude	22.3	-	61.1	-
CS-1	Clarson	24.2	-	-	58.1
Alt-4	Exshaw	18.5	15.1	48.4	-
Alt-5	Exshaw	18.0	16.2	54.8	-

EFFECT OF PARTICLE SIZE

Other than screening through a 0.149 mm (100 M) sieve, no attempt was made to size the material used to make pellets. As can be seen from Table 3 and also from Table 1 there is an appreciable variation in the average particle size and size distribution of the ground material. These variations reflect the differences in the physical nature of the rocks. To evaluate the effect of material particle size, two dolomites, NS-2 and NB-3, were ground in a disc pulverizer, a portion removed for pelletizing and the remainder ground a second time. Figure 2 shows that for pellets of this material there is a considerable improvement in sulphation with the reduced particle size. The finer material was easier to pelletize and produced stronger pellets than the coarser size. Being stronger there may be less loss due to attrition, which could account in part for the higher sulphation capacity. It is probable that there is an economical optimum size to which a limestone should be ground, since grinding costs increase with decreasing particle size. In a large scale operation size reduction of the limestone would be accomplished with jaw, cone or gyratory crushers followed by perhaps a hammermill and then a ball mill. The size distribution of the limestone would be no doubt different than in these tests. Therefore, these sulphation capacity results should be considered as indicative of expected performance of finely ground material rather than as absolute values.

EFFECT OF PELLET SIZE

Sulphation tests were conducted on pellets sieved at 0.841-1.00 mm as this is the standard size for this procedure. In order to determine whether pellet size had an effect on sulphation, a series was run with Gays River tailings pellets and also the Glencoe, NS-6 pellets. The results, Table 4, were somewhat surprising as they showed that the largest pellets gave the highest results. A possible explanation for these results is that the smaller pellets are weaker and more susceptible to attrition and subsequent loss of material. It would appear that the larger pellets are sufficiently porous that increasing size does not offer resistance to sulphation. That is, the sulphation reaction is essentially independent of pellet size.

TABLE 4. Sulphation capacity versus pellet size

Sample	Sieve size mm		
	.841-1.00	.595-.841	.297-.595
Gay's River	87.5	74.7	72.7
Glencoe	40.6	41.6	36.3

HYDRATION OF SULPHATED LIMESTONE

The results of the preliminary hydration enhancement experiments are very encouraging. The samples were sulphated, hydrated, and sulphated a second time. The degree of the initial sulphation was not measured, nor was the extent of hydration. The sulphation capacities given in Table 5 are calculated from the chemical analysis of calcium and sulphur in the resulphated bed material. For comparison purposes the previously determined sulphation capacities of the limestone are also given. All samples indicate a substantial increase in sulphation capacity; NS-6 showing more than three times the initial capacity.

TABLE 5. Hydration enhancement of sulphation capacity

Limestone	Rock % sulphation	Hydrated Sample % sulphation
NS-5	31.6	50.8
NS-6	21.3	69.2
NS-7	20.3	53.3
NS-9	23.2	64.7
NS-11	19.6	45.5
NB-1	30.6	59.9

A 30-g sample of NB-1 was sulphated, the sulphation capacity being calculated to be 34%. Chemical analysis of the bed material for Ca and S resulted in a sulphation conversion of 40.5%. It should be noted that the chemical analysis of the bed material generally results in higher sulphation than that calculated from the emission curves. Part of the difference may be attributable to attrition and dust loss which would result in lower overall calculated sulphation.

The sulphated sample was placed in water for 24 h and then allowed to air dry for three days. A portion of this hydrated material when heated to 625°C gave a weight loss of 11.2% which was assumed to be the water

content. If all of this weight loss were water of hydration, then calculations indicate that the unsulphated lime was hydrated to 88%. The hydrated sample was resulphated and the bed material analysed. From the sulphation curves, the overall sulphation was calculated as 55%. The chemical analysis of the bed material gave 70% conversion.

A potential problem with the hydration method of improving sulphation capacity is in the physical nature of the hydrated rock. As water reacts with the CaO to form $Ca(OH)_2$ the particle swells and cracks (2). If the sample is resulphated soon after hydrating, the method works very well. However, if there is a time delay of weeks before the material is reused, the hydration reaction appears to continue and the particle becomes very soft and powdery. This effect may even be observed with sulphated bed material which has been stored in an open container and allowed to absorb moisture from the air. Reinjection of this type of "over-reacted" material into the FBC would result in excessive attrition and loss of material by eleutriation.

SULPHATED BED MATERIAL

Several samples of bed material, composed of ash and partially sulphated lime, were obtained from the start-up operation at CFB Summerside. One sample, SA-4, is from CCRL and was diluted with sand. In all cases the initial limestone feed was Havelock, NB-1. The calcium analysis of the Summerside FBC bed material indicates that it contains less than 30% ash. The samples were tested in the FBR after fine grinding and pelletizing with bentonite and sodium carbonate. The initial degree of sulphation was determined by chemical analysis on the pellets and is given as mol % S/Ca. The sulphation of the remaining unreacted calcium is given as X%. The overall sulphation is the combination of the two. The results are given in Table 6.

With the exception of SA-3, the sulphation of the lime in the recycled material exceeded that of the unreacted rock. That is, the overall sulphation was more than twice that of the once-through limestone. Sodium carbonate was the preferred binder, although if fresh material had been available, it is unlikely that any binder would have been required. Although these tests used only bed material, cyclone and bag house dust could also be incorporated as pellets. This has the added advantage of recycling unreacted carbon to the combustor. Pellets of partially

sulphated lime would be used in a different combustion stage or bed to that for fresh limestone in order to separate the two.

TABLE 6. Sulphation capacity of pelletized spent bed material

Sample	Chemical Analysis			X%	Total	Binder
	%CA	%S	mol% S/CA			
SA-1	39.27	8.55	27.2	34.9	62.1	2% ben
SA-1				38.4	65.6	5% Na_2CO_3
SA-2	35.38	9.07	32.0	39.9	71.9	2% ben
SA-2				46.4	78.4	5% Na_2CO_3
SA-3	45.52	10.63	29.2	21.9	51.1	5% Na_2CO_3
SA-4	15.38	2.56	20.8	55.7	76.5	5% Na_2CO_3

Model Prediction of Pellet Useage

The sulphation equation parameters for the tests performed with bentonite and sodium carbonate binders are given as Tables 7 and 8.

TABLE 7. Sulphation parameters of 0.841-1.00 mm pellets made from -0.149 mm carbonate rocks with 2% bentonite binder
$X\% = a[1-\exp(-kt^n)]$

Sample	Test	X%	a	k	n	P(Vol SO_2) (mL/m^3)
NS-1	268	40.86	40.797	.03422	1.1141	2700
NS-9	248	36.49	36.562	.04307	1.1104	2750
NS-4	276	58.58	58.942	.02497	1.1832	2700
NS-8	247	61.24	60.732	.02431	1.1513	2750
NS-5	278	52.40	53.910	.02476	1.1362	2550
NS-6	354	40.65	40.871	.04386	1.0813	2500
NS-7	168	33.94	34.159	.04403	1.1345	2700
NS-11	201	33.39	33.322	.04260	1.1745	2700
GR	237	77.48	79.280	.07645	.7310	2750
NB-1	164	35.55	34.956	.04752	1.1464	2650
NB-3	279	28.66	28.581	.08516	1.2338	2650
NB-4	277	40.72	39.966	.03922	1.1624	2650
NB-5	280	41.97	41.914	.03239	1.1776	2750
SY-2	349	48.06	53.009	.04340	.8463	2550
Alt-4	296	48.37	49.606	.03424	1.0331	2600
Alt-5	300	58.64	59.879	.02464	1.0889	2700

TABLE 8. Sulphation parameters of 0.841-1.00 mm pellets made from -0.149 mm carbonate rocks with 5% Na_2CO_3 binder
$X\% = a[1-\exp(-kt^n)]$

Sample	Test	X%	a	k	n	P(Vol SO_2) (mL/m^3)
NS-2	316	37.54	37.108	.13058	0.95533	2650
NS-4	322	67.95	71.427	.02434	1.1261	2800
NS-8	319	67.23	69.008	.02074	1.236	2600
NS-5	311	50.73	51.118	.03386	1.1936	2700
NS-6	328	33.63	33.684	.06410	1.1978	2650
NS-7	324	47.00	47.552	.02736	1.3108	2650
NS-9	337	56.60	57.624	.02683	1.0993	2625
NB-1	293	57.43	57.649	.02456	1.1997	2700
NB-2	323	58.97	59.017	.02828	1.1645	2650
NB-3	336	65.66	65.111	.07048	1.0233	2625
NB-4	325	63.51	64.261	.02170	1.2031	2600
NB-5	327	67.10	66.921	.02183	1.1806	2600
GR	312	87.51	88.836	.04015	1.0914	2650
CS-1	333	58.07	61.089	.02831	1.1142	2650

The parameter "a" in Equation 1 closely approximates the maximum value of the sulphation capacity for the material. The values of "k" are generally smaller than the values for the equivalent natural rock. The values of "n" are considerably higher, averaging 1.1 compared to 0.79 for the rock. For n=1, the rate of calcium utilization decreases linearly as the extent of calcium utilization increases; for other values of n, the rate decreases but not linearly.

In order to compare the predicted performance of pellets versus natural rock the fluidized bed reactor data were used in the ANL model along with the physical parameters of the Summerside AFBC unit. The operating conditions for the AFBC are given in Table 9. Descriptions of the model are in references 6 and 7.

TABLE 9. Summerside AFBC operating conditions

Temperature = 850°C
Pressure = 101 kPa
Fluidizing velocity = 1.83 m/s
Static bed height = 0.6 m
Expanded bed height = 1.5 m
Area of bed = 3.52 sq m (A bed), 3.96 sq m (B bed)
Number of openings in distributor = 284 (A bed), 472 (B bed)
Coal feed rate = 1100 kg/h
Sulphur content in coal = 4.1%
Sorbent particle size = 6*20 Mesh; ave 1.24 mm
Sorbent density = approx. 1.1 g/cc (bulk), approx. 2.5 g/cc (particle)

Some graphs of the predicted performance of the sorbents as natural rock and as pellets are presented in Figure 3 to 7. The results are quite dramatic, the quantity of sorbent in pellet form required to achieve 80-90% SO_2 capture is a factor of at least two, and occasionally up to five times less than that required as natural rock. There is a tendency for the poorer natural sorbents to show the greater improvement than the better sorbents when finely ground and pelletized. Thus the Brookfield limestone, NS-4 and -8, which were among the worst sorbents as natural rock, perform slightly better than Calpo limestone pellets, NS-5 and -10, which are the best natural sorbents, Figure 3. For most of the pellet samples 90% SO_2 retention is possible with a Ca/S ratio of 2.0-2.5. These Ca/S ratios are in line with published results for fast recirculating fluidized units using finely ground limestone (8).

ECONOMIC EVALUATION OF PELLETIZATION

To produce pellets of finely ground limestone would require additional, costly process operations of ball milling and pelletizing. In order to determine whether this expense is justified by the savings in equipment and material, an economic evaluation was conducted by J. Palmer of MSL's Technical and Economic Evaluation Section. For this evaluation it was assumed that a 150 MW (electrical), which is equivalent to a 375 MW (thermal), FBC unit would be built at Point Tupper, NS. At 100% operation such a unit would burn 400,000 t/y coal rated at 30 MJ/kg and containing 4% sulphur. Limestone for SO_2 capture would probably be quarried from the Glencoe deposit approximately 80 km from the power plant. This deposit has indicated quarryable reserves of 345 million tonnes of metallurgical and cement grade limestone (9). The reserves of other deposits, Irish Cove and Calpo, which are within a reasonable distance from the power plant, are insufficient to supply the plant for more than a few years.

The Glencoe limestone is not a particularly good sorbent. The sulphation capacity of the rock is about 20%. In pellet form the capacity varies from 33 to 47% depending upon the average particle size and the binder type. Model predictions, based on the Summerside FBC data, and assuming 90% SO_2 retention from combustion of a 4.1% S fuel are given in Figure 3. This graph would indicate a required Ca/S ratio of approximately 6 for coarse rock, and from 3 to 2 for pellets. Expressed as weight, the

natural rock requirement would be in the order of 1 kg/kg coal, whereas the pellet requirement would be 0.5 to 0.33 kg/kg coal. The curves for the proposed plant may vary from those shown depending upon the operating parameters and limestone particle size, however the relative difference between the rock and pellets should be the similar.

The two evaluated cases were:

Case 1: To quarry, transport and crush to -6.3 mm an annual requirement of 400,000 t/y limestone for Ca/S ratio of 6.

Case 2: To quarry, transport, crush and pulverize to -0.149 mm and then pelletize an annual requirement of 200,000 t/y limestone for Ca/S ratio of 3.

Capital Costs:

Case 1:		
Crushing equipment, 400,000 t/y -6.3 mm, operating 3 shifts, 5 days/week	=	$6,208,527
Transportation, 15 trucks of 40 t capacity, operating 1 shift, 5 days/week	=	$1,760,000
Total Capital	=	$7,968,527
Case 2:		
Crushing, ball mill and pelletizing equipment, 200,000 t/y, operating 3 shifts, 5 days/week	=	$ 938,667
Total Capital	=	$8,180,974

Operating Costs $/Tonne Limestone:	Case 1	Case 2
Transportation - including fuel, labour, maintenance operating supplies, indirect and fixed costs	$ 5.54	$ 5.54
Communition - raw materials, utilities, labour, maintenance, supplies, indirect and fixed costs	$ 8.89	$18.85
Cost of capital investment at 12%	$ 2.39	$ 4.91
Total Operating	$16.82	$29.30

A third case for a Ca/S ratio of 2 may be approximated by proportioning the costs in Case 2. Case 3 would require the quarrying, crushing, pelletizing, etc., of 132,000 t/y limestone.

Total annual limestone cost:	Case 1	$6,728,000
	Case 2	$5,860,000
	Case 3	$3,862,600

The calculated cost of limestone sorbent for SO_2 control is a significant portion of the operating cost of an FBC unit burning high sulphur coal. With the quantity of limestone required as pellets being one half to one third that of natural stone there is considerable cost advantage with the pellet method. The saving in waste disposal cost associated with the smaller quantity of material with pellets use was not included in the calculations. Most of the difference in operating costs of the two cases is due to the ball milling operation to produce finely ground limestone. The pelletizing operation accounts for about $2/tonne of the operating cost. Thus if the proposed FBC unit were of the fast recirculating type, which utilizes fine limestone, a small additional cost saving would be realized.

CONCLUSION

Several techniques for improving the utilization of limestone in AFBC use were investigated in a bench scale FBR. The use of pelletized fine particle material greatly improves the sulphation capacity and reduces the Ca/S ratio required for SO_2 capture when compared to the usual sized rock used. An economic evaluation indicates a cost saving with pellets. It is believed that the superior results obtained for pellets are indicative of the behaviour that would be expected for finely ground limestone in a circulating FBC.

Preliminary experiments showed that either hydration of sulphated bed material or the grinding and pelletizing of this material could considerably improve, by a factor of two or more, the utilization of sorbents in an AFBC.

ACKNOWLEDGEMENTS

The preparation of samples and the operation of the test reactor were capably done by my technician, N. Roxburgh and R. Brulotte, Waterloo University Co-op student. Chemical analyses were performed by J.C. Hole and R.R. Craig. The economic evaluation was conducted by J. Palmer.

REFERENCES

1. Hamer, C.A. "SO_2 sorbent utilization in fluidized beds"; Division Report ERP/MSL 83-6 (IR); CANMET, Energy, Mines and Resources Canada; July 1983.
2. Shearer, J.A., Smith, G.W., Myles, K.M., Johnson, I. "Hydration enhanced sulfation of limestone and dolomite in the fluidized-bed combustion of coal"; J Air Pollution Control Assoc 30:6:684-688; June 1980.
3. Tonry, J.R. "Pelletizing in cement manufacturing"; Int'l Sym AIME; edited W.A. Knepper; April 12-14, 1961 Phil; Interscience.
4. Van Houte, G., Delmon, B., Maon, J.C., Dumont, P. "Desulfurization of flue gas in a fluidized-bed of modified limestone"; J Air Pollution Control Assoc 28:10:1030-1033; Oct. 1978.
5. Smith, G.W., Lenc, J.F., Shearer, J.A., Chopra, O.K., Myles, K.M., Johnson, I. "Influence of salts on the sulfur retention of limestone in atmospheric fluidized-bed combustors"; ANL/CEN/FE-80-19; Argonne National Laboratory, Illinois; 1980.
6. Fee, D.C., Myles, K.M., Wilson, W.I., Fan, L.S., Smith, G.W., Wong, S.H., Shearer, J.A., Lenc, J.F., Johnson, I. "Sulfur control in fluidized-bed combustors: methodology for predicting the performance of limestone and dolomite sorbents"; ANL/FE-80-10; Argonne National Laboratory, Illinois, Sept. 1982.
7. Fee, D.C., Wilson, W.I., Myles, K.M., Johnson, I. "Fluidized-bed coal combustion: in-bed sorbent sulfation model"; Chem Eng Sci 38:11:1917; 1983.
8. Friedrich, F.D., Lee, G.K., Desai, D.L., Kuivalainen, R. "Fluidized bed combustion of petroleum coke"; ASME Joint Power Generation Conf, Denver, Colorado, Oct. 1982.
9. MacNeil, D.J. "The Glencoe limestone and dolomite survey"; N.S. Dept of Mines, May 1976.

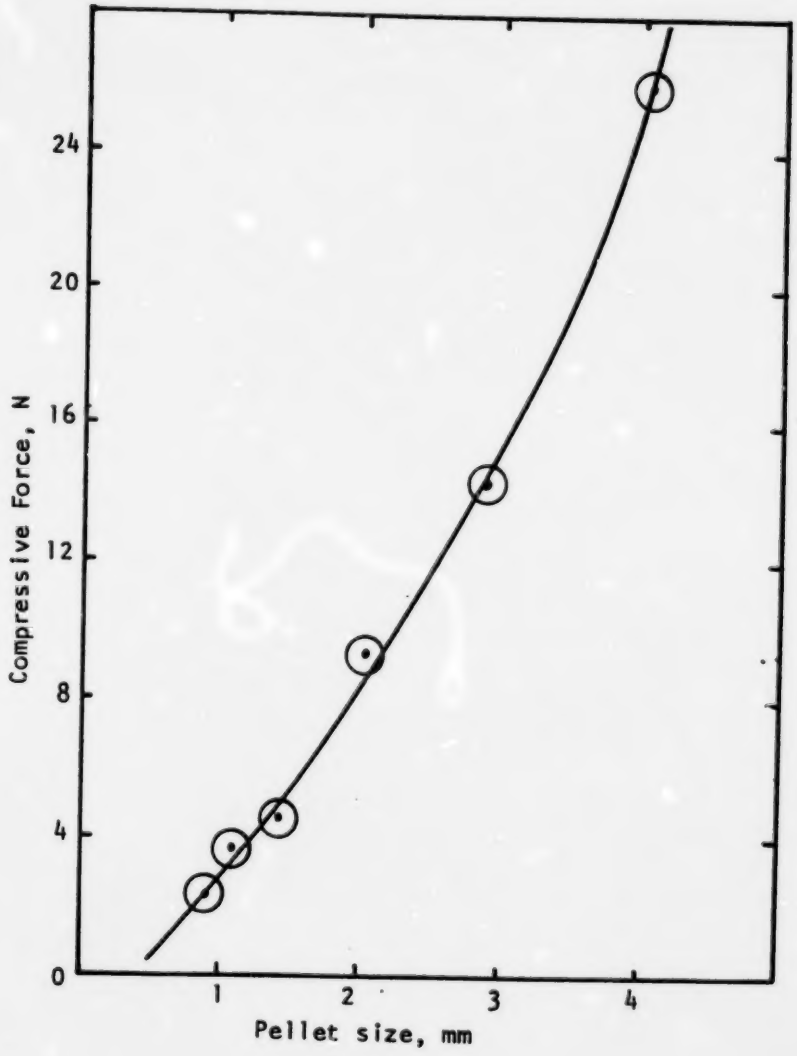


Fig. 1 - Crushing strength, newtons, versus average pellet diameter for Havelock limestone with 15% quick-set cement binder

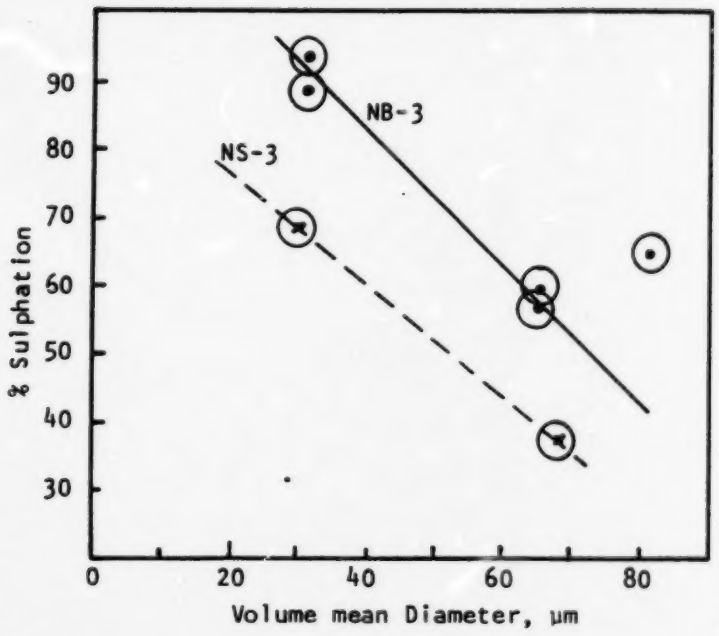


Fig. 2 - Effect of particle size on sulphation of dolomite pellets

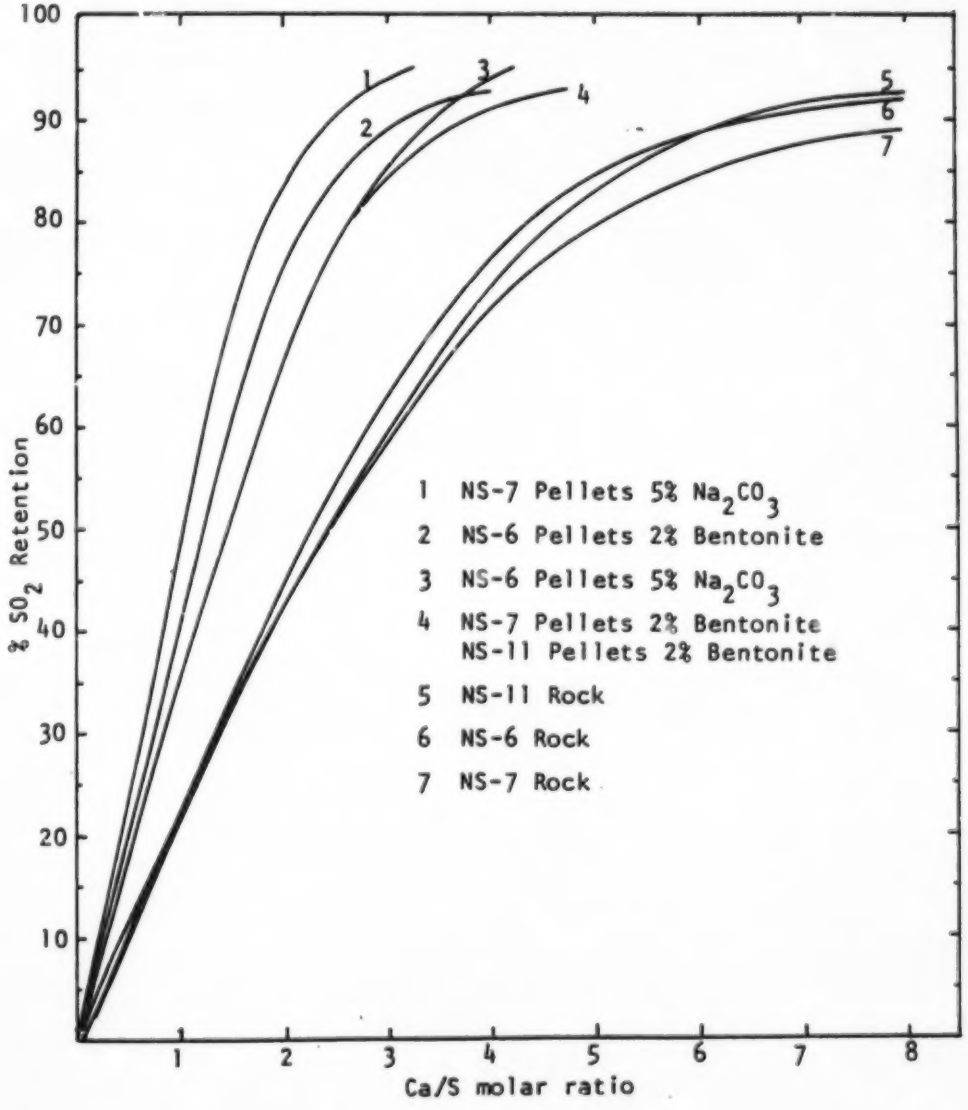


Fig. 3 - Predicted performance of Nova Scotia sorbents - rocks and pellets - in the Summerside AFBC burning 4.1% fuel

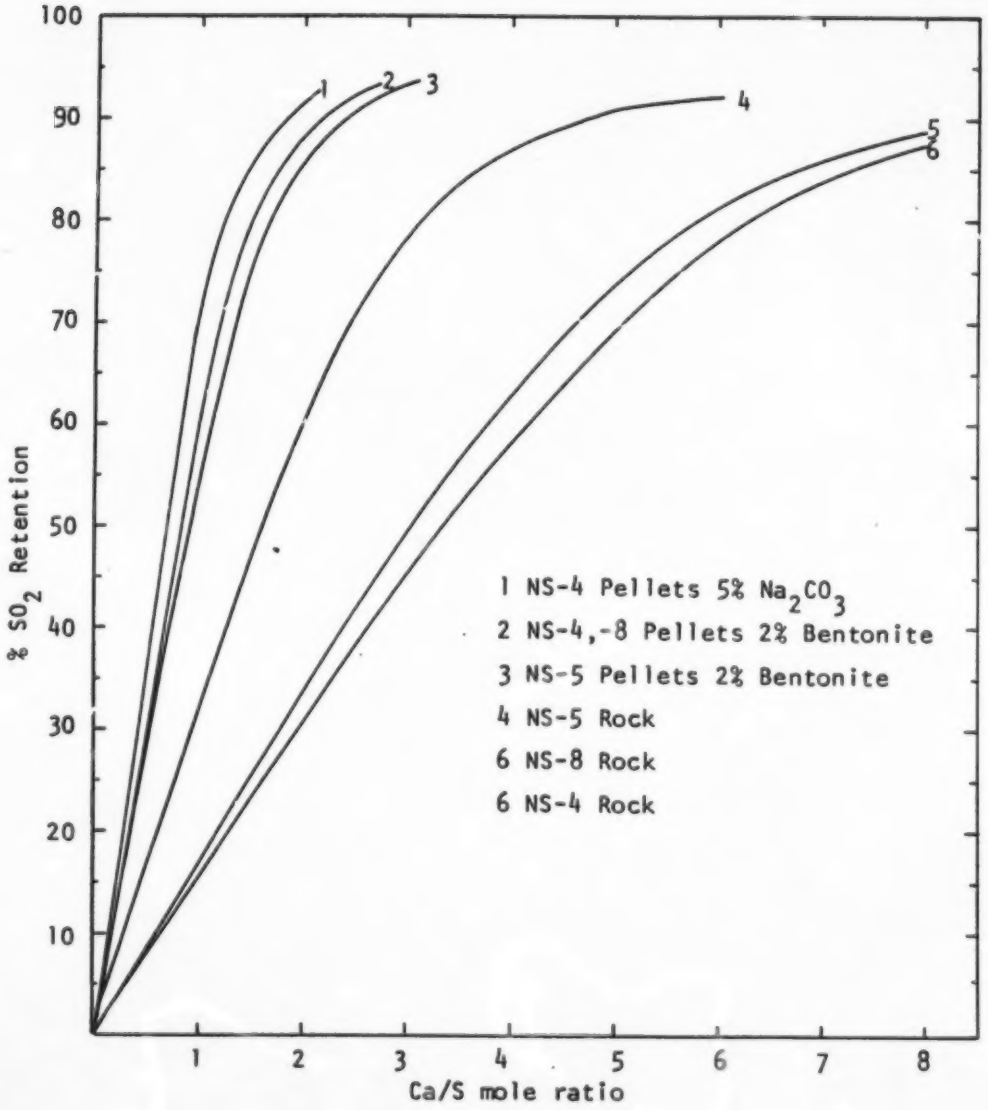


Fig. 4 - Predicted performance of Nova Scotia sorbents - rocks and pellets - in the Summerside AFBC burning 4.1% fuel

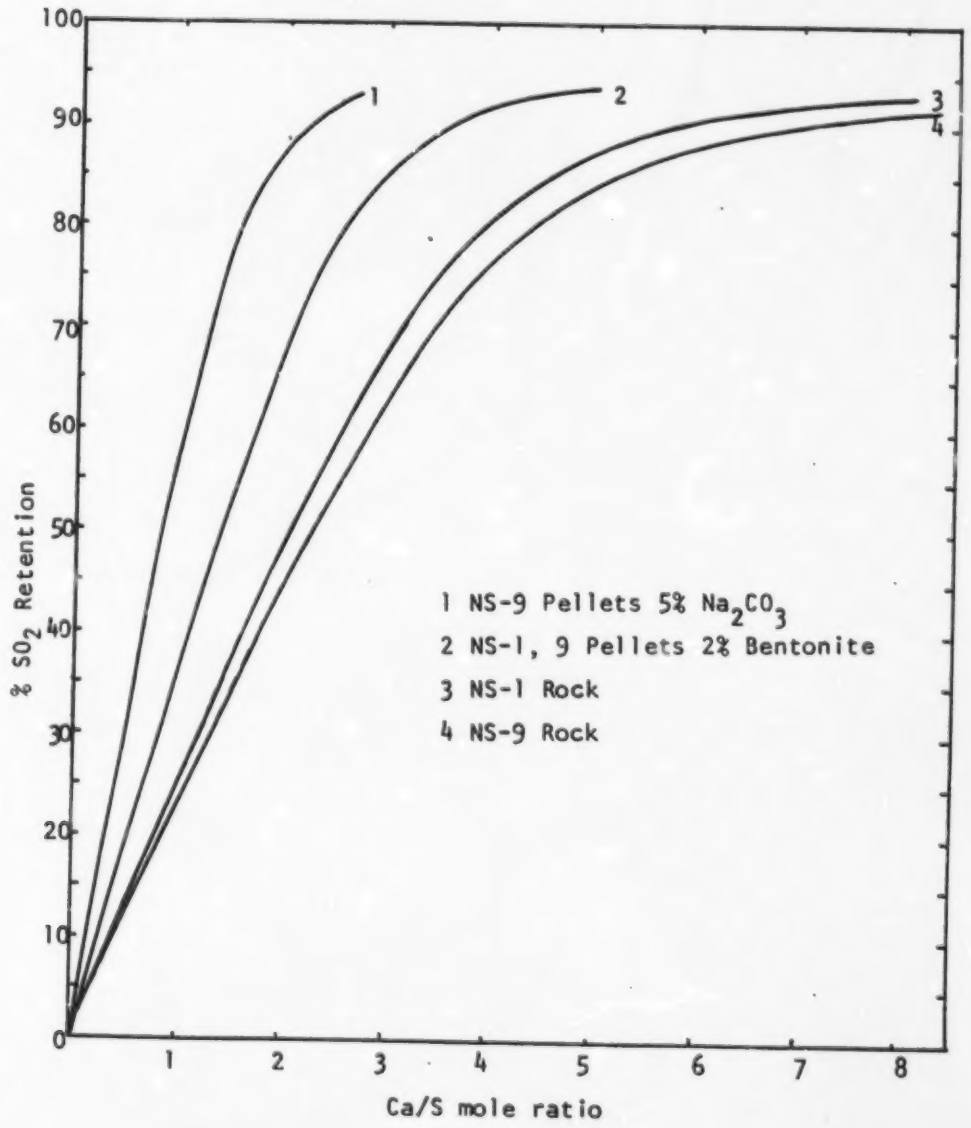


Fig. 5 - Predicted performance of Nova Scotia sorbents - rocks and pellets - in the Summerside AFBC burning 4.1% fuel

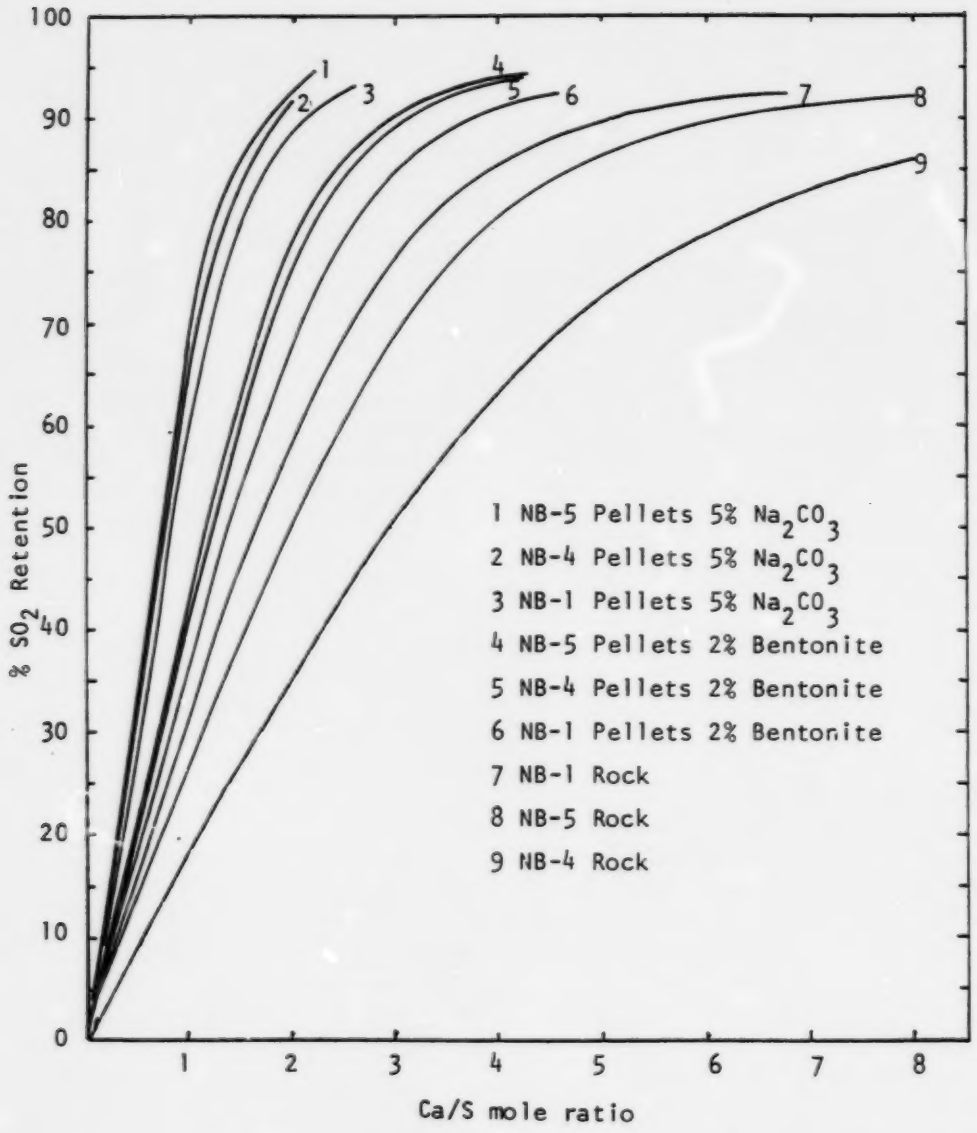


Fig. 6 - Predicted performance of New Brunswick sorbents - rocks and pellets - in the Summerside AFBC burning 4.1% fuel

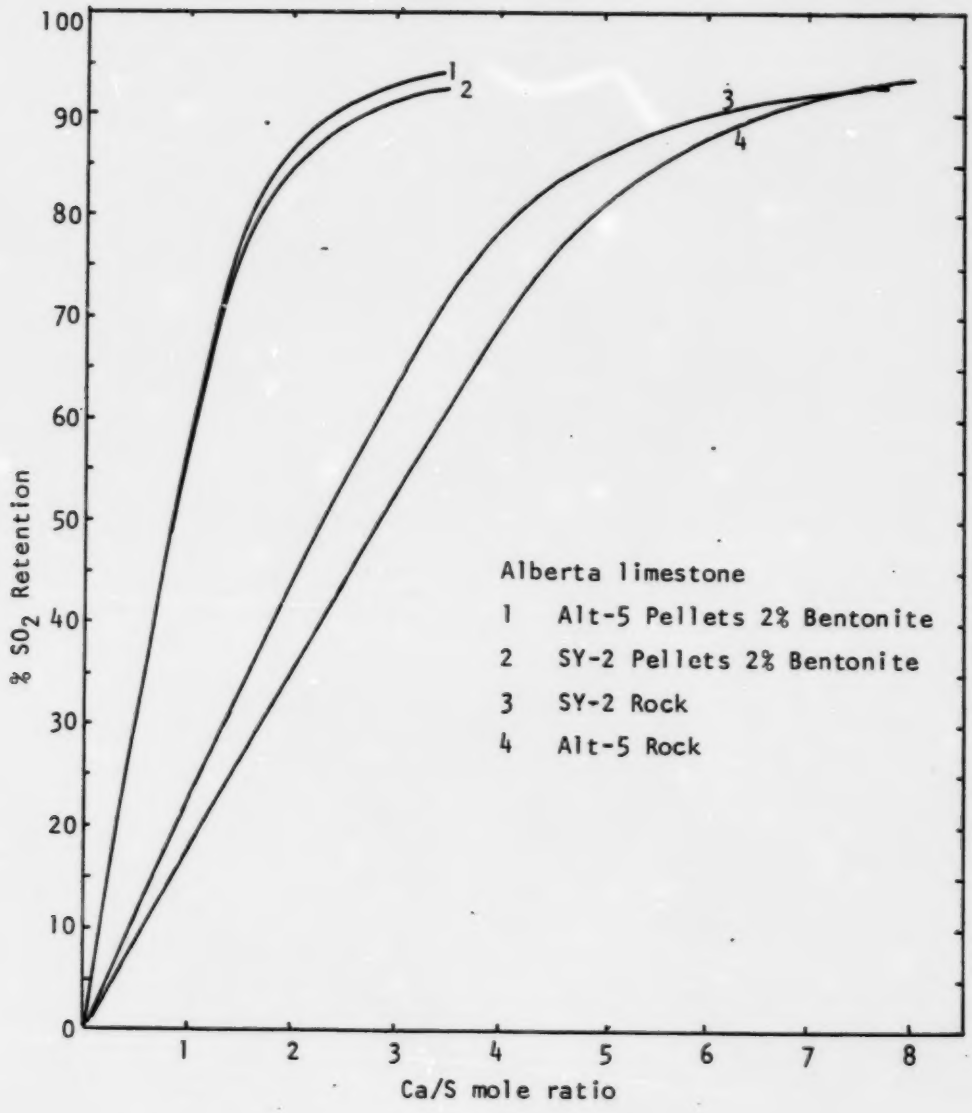


Fig. 7 - Predicted performance of Alberta sorbents - rocks and pellets - in the Summerside AFBC burning 4.1% fuel